RATES OF REACTIONS

Chapter 15

The concept of "**rate**" indicates how fast a certain activity takes place over time. The 'rate of a chemical reaction' refers to the change in concentration of a substance in a chemical reaction in a given unit of time. During a chemical reaction, the amounts of reactants decrease over time and the amounts of the products increase over time. This rate can determined at any stage of the reaction. A study of the rates of chemical reaction is called **chemical kinetics**.

Key Ideas

Fast and slow reactions

1. Each chemical reaction has its own rate. Some are fast and some are slow. The major factors influencing the rate of a reaction are the concentration, physical state and the temperature.
2. Concentration affects rate by influencing the frequency of collisions between reactant molecules, and the physical state of the substance affects the rate by determining the surface area per unit volume of molecules. Temperature affects rate by influencing the frequency and the energy of collisions.

The rate equation

3. The average reaction rate is the change in the reactant or product concentration over change in time. The rate slows as reactants are used up.
4. Example: N_2O_5 decomposes in a solvent such as carbon tetrachloride : $2N_2O_5 \rightarrow 4NO_2 + O_2$. The rate of this reaction in any interval of time can be expressed as the change in concentration of N_2O_5 divided by the change in time:

   Rate of reaction = [(change on $[N_2O_5]$) ÷ (change in time)] = $-\Delta[N_2O_5] \div \Delta t$.

   The **minus** sign is generally used because the concentration of N_2O_5 decreases with time. But, the rate is always expressed as a positive quantity. The rate could also be expressed in terms of the rate of formation of NO_2 or O_2. The rates expressed in these ways will always have positive sign because the concentration is increasing.

   Rate = $-\Delta(N_2O_5) \div \Delta t$; or, Rate = $\Delta(NO_2) \div \Delta t$: or, Rate = $\Delta(O_2) \div \Delta t$

Collision theory

5. Chemical reactions can be described by the collision model that assumes that molecules must collide in order to react. A certain minimum energy, called the **activation energy** (E_a) is necessary for a collision to form products. Increasing the temperature of a reaction increases the average speed of the molecules and their collision frequency. Only those collisions with enough energy can lead to reaction. At high temperatures, most effective collisions occur and the rate increases.
6. Molecules should also collide with a certain orientation in order to be effective. Head-on collisions with the required activation energy are most effective.
7. As a reaction progresses, it reaches a transition state where the kinetic energy of the particles change into potential energy during a collision. Given adequate energy and correct orientation of collision, the reacting species reach an unstable state called the **transition complex** and decomposes into either the reactants or the products.

Catalysts

8. The path of most reactions consists of two or more steps. One of these steps is the **rate-determining step** or rate limiting step which is the slowest. This step determines how fast the overall reaction occurs.

9. A catalyst is a substance that speeds up a reaction without being consumed. A catalyst operates by providing a lower-energy pathway for the reaction. A typical catalyst can increase the reaction rate by a factor of as much as 1.0×10^7 to 1.0×10^{14}. **Enzymes** are biological catalysts. These substances speed up the rate determining step in a reaction.

10. Example: The rate of decomposition of H_2O_2 is increased by the addition of MnO_2 as a catalyst. The rate of production of NH_3 in the Haber Process is increased by the use of Fe/FeO as catalysts.

11. **Biological catalysts** (enzymes): The enzymes trypsin, chymotrypsin and elastase are digestive enzymes. These are produced in the pancreas and secreted into the digestive tract. Acetylchlorinesterase is involved in speeding nerve impulses. The enzyme glucose phosphatase has the role of maintaining the glucose level in the blood.

Catalytic converter:

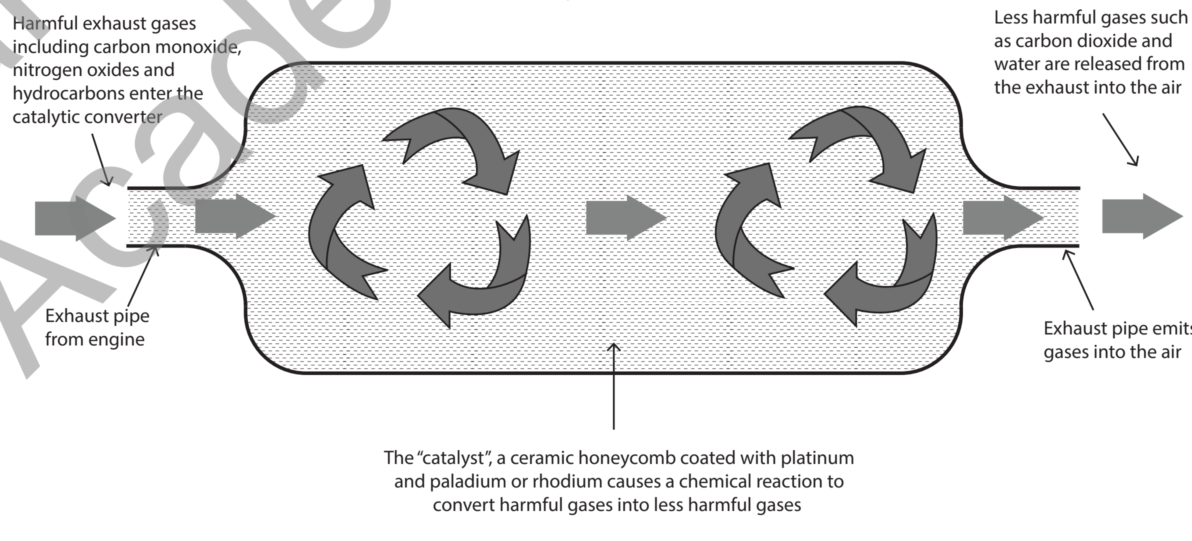
12. This is a device used to reduce the toxicity of emissions from an internal combustion engine such as in an automobile. It works by using a catalyst to stimulate a chemical reaction in which the toxic by-products of combustion are converted to less toxic substances.

13. In automobiles, this typically results in 90% conversion of carbon monoxide, hydrocarbons and nitrogen oxides to less harmful gases: Unburnt hydrocarbons contribute to smog which is poisonous to lung breathing animals. Carbon monoxides and nitrogen oxides contribute heavily to air pollution and acid rain. In the "CATCON" these are converted as follows: CO to CO_2; unburnt hydrocarbons to CO_2 and H_20; and, nitrogen oxides to nitrogen and oxygen gas.

    The exhaust gases are purified as they pass through the converter before exiting the vehicle exhaust system.

14. In a catalytic converter, the catalyst (in the form of platinum or molebdenum is coated on a ceramic honeycomb or ceramic beads in a muffler like package attached to the exhaust pipe. The catalyst helps to make the conversion to less harmful gases.

Catalytic Converter (CATCON)



Reaction rates and molecular bonds

12. Reactions where bonds are to be broken and reformed are much slower than reactions involving ions. Thus the reaction, $Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$ is faster due to the electrostatic attraction between the oppositely charged ions.

13. A reaction such as $N_2(g) + O_2(g) \rightarrow 2NO(g)$ is a slow reaction because of the energy involved in breaking the bonds within nitrogen and oxygen molecules and the bonds to be reformed within the molecules of NO.

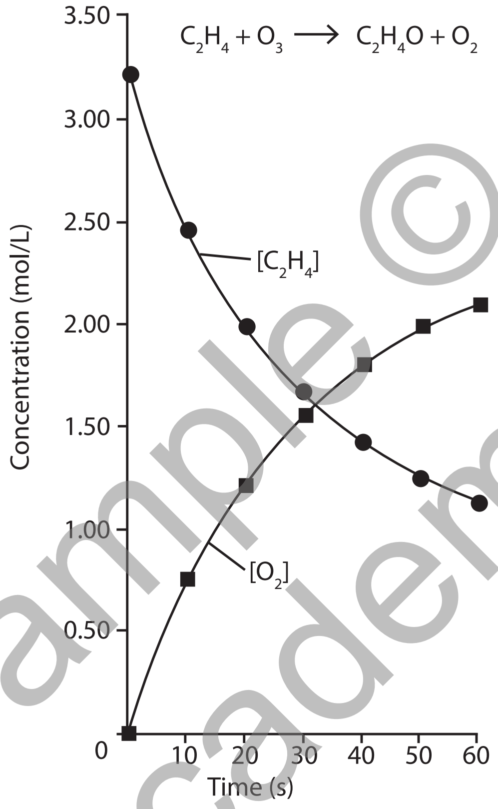
Energy in a chemical system

14. The total energy within a chemical system is constant. This means that energy can be transformed from one type to another, but the total energy within a system will remain the same.

15. Energy changes in exothermic and endothermic processes: All bonding essentially results from the attraction between positively charged particles and negatively charged particles. When bonds are broker or formed, the energy of the bonding arrangements changes. If the particles are forced apart, work is done on the system. The energy transferred to the system is stored as available potential energy. If the particles come together again, the stored energy is released.

Chemical Equilibrium

16. When a chemical reaction is carried out in a closed vessel, the system achieves chemical equilibrium – the state where the concentration of both reactants and products remain constant over time.

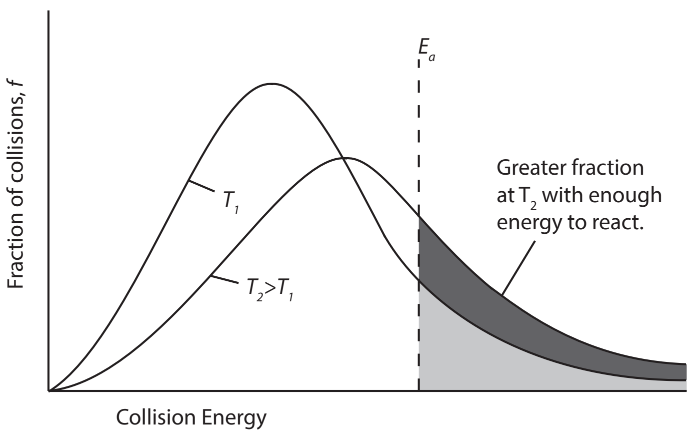


Plots of $[C_2H_4]$ and O_2 vs Time

Measuring reactant $[C_2H_4]$ and product $[O_2]$ gives curves of identical shape changing in opposite directions. The steep upward (positive) slope of $[O_2]$ early in the reaction mirrors the steep downward (negative) slope of $[C_2H_4]$ because the faster C_2H_4 is used up, the faster O_2 is formed. The curve shapes are identical in this case because the equation coefficients are identical.

The effect of temperature on the distribution of collision energies

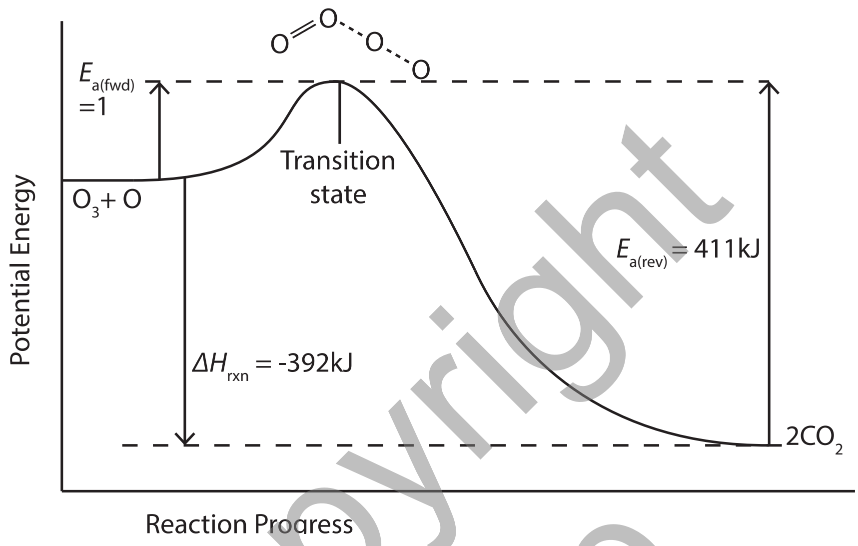
An increased temperature increases the number of particles which are able to react as they go above the activation energy barrier..



Reaction energy diagram and the transition state for the reaction

$O_3 + O \rightarrow 2CO_2$

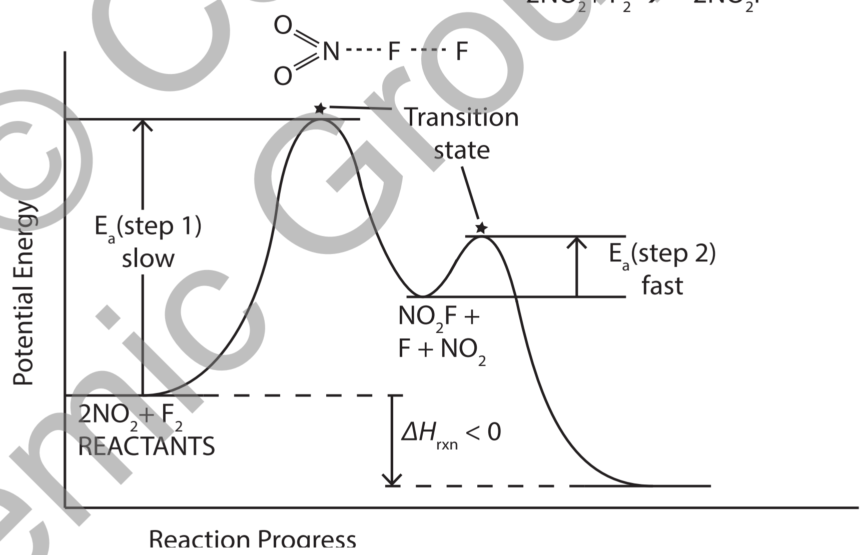
The activation energy for the reverse reaction is the sum of the Ea for the forward reaction plus the heat of reaction for the forward reaction.



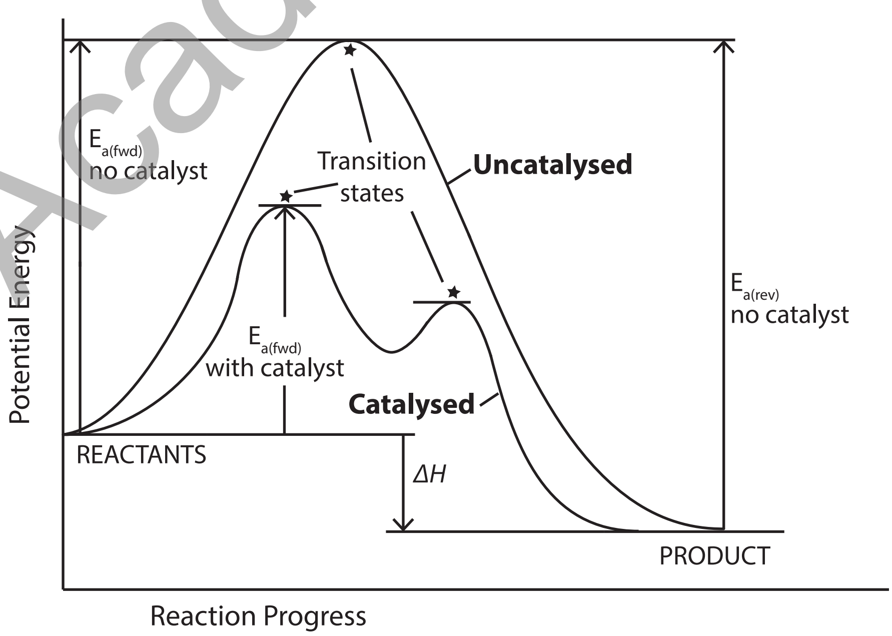
Reaction energy diagram and the transition state for the reaction

$2NO_2 + F_2 \rightarrow 2NO_2F$

A reaction may contain two or more steps..



Reaction energy diagram of a catalysed and uncatalysed reaction



A catalyst speeds a reaction by providing a new lower energy pathway. In this case by replacing the one-step mechanism with a two-step mechanism. Both forward and reverse rates are increased to the same extent, so a catalyst does not affect the overall reaction yield. (The only activation energy shown for the catalysed reaction is the larger one for the forward direction.)

EXERCISES AND PROBLEMS

1. For the reaction, $H_2(g) + Br_2(g) \rightarrow 2HBr(g)$, list the types of bond that must be broken and the types of bond that must form in order for the chemical reaction to take place.

2. For the reaction, $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$, list the types of bonds that must be broken and the types of bonds that must form in order for the chemical reaction to take place.

3. What does the activation energy for a reaction represent? How is the activation energy related to whether a collision between molecules is successful?

4. What are catalysts in living cells called? Why are these biological catalysts necessary?

5. What are the factors that will affect the total amount of solute that can dissolve in a given amount of solvent?

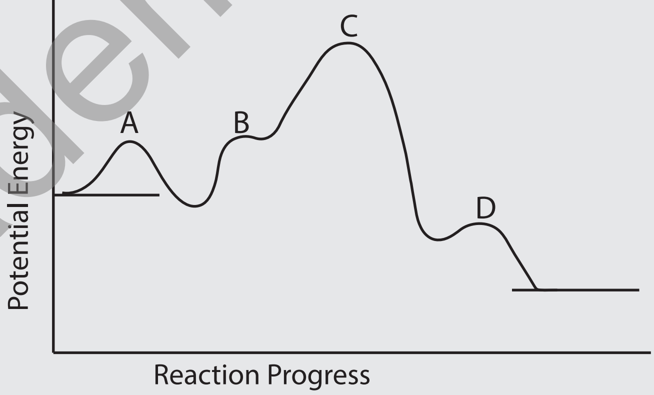
6. What is the central idea of the collision theory? How does this relate to the effect of concentration on collision rate?

7. For the reaction, $A_2 + B_2 \rightarrow 2AB$, E_a (forward) = 125 kJ mol^{-1} and E_a (reverse) = 85 kJ mol^{-1}, draw a reaction profile diagram.

8. Does a catalyst increase the reaction rate the same way as a rise in temperature does?

Explain.

9. Consider the energy profile diagram here.



a) How many elementary steps are in the reaction mechanism?

b) Which step is limiting?

10. Suggest an experimental method for measuring the change in concentration with time for each of the following reactions:

a) $CH_3CH_2Br(l) + H_2O(l) \rightarrow CH_3CH_2OH(l) + HBr(aq)$

b) $2NO(g) + Cl_2(g) \rightarrow 2NOCl(g)$

11. Read the following statements describing what happens in various situations. Provide very brief explanations using short key words or terms.

a) Explosions occur in flour mills where flour is stored in large containers.

b) Some ways by which the rate of combustion of a candle can be increased.

c) Starch in the form of sugar requires a very high temperature to burn. However, in the cells of a living organism it occurs at a low temperature.

d) Catalysts are preferred to speed up many industrial chemical reactions compared to using high temperatures.

e) Explosion will occur when container of nitroglycerine is tossed up in the air. But, it is relatively safe when stored in a shelf.

f) Rust inhibitors are used in the car radiators. They can be called negative catalysts.

g) It takes a long time to cook meat in an open container. It takes a short time to cook it a pressure cooker.

h) Magnesium ribbon pieces are reacted with dilute hydrochloric acid to produce hydrogen rather than magnesium powder.

i) Oxy-hydrogen welding torches are much hotter than air-hydrogen torches.

j) Milk becomes sour when kept at room temperature.

k) Many organic cleaning agents are more effective in hot water rather than in cold water.

l) A glowing splint does not burst into flame when held in air. But, when it is introduced in to a jar of oxygen, it bursts into flame almost instantaneously.

MULTIPLE CHOICE QUESTIONS

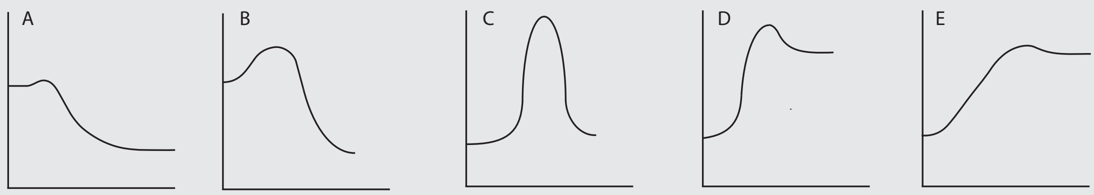
1. A substance **X** is added to a substance **Y** to produce a new substance **XY**. A thermometer placed in the insulated reaction vessel records a temperature rise. From this observation we can infer that

   a) the total stored energy of the **XY** particles is less than the total stored energy in the **X** and **Y** particles.

   b) the total stored energy of the **XY** particles is no different from that of **X** and **Y** particles before reaction, but the kinetic energy of the **XY** particles is higher.

   c) the surroundings have given up energy to the reacting particles.

   d) no conclusion can be reached concerning energy changes as the number of moles of **X, Y** and **XY** is not given.



2. The following equation represents the dissolution of potassium iodide in excess water.

   $KI(s) \rightarrow K^+(aq) + I^-(aq)$ $\Delta H = +20.5$ kJ

When a sample of potassium iodide is dissolved in excess water,

a) the temperature of the water will begin to rise because of the reaction.

b) the temperature of the water will remain the same but heat will immediately be taken in from the surroundings.

c) the water will become colder because of the reaction.

d) heat will be given off to the surroundings and the temperature of the water will fall.

3. Consider the following equation:

$2Al(s) + 6HCl(aq) \rightarrow 2AlCl_3(aq) + 3H_2(g)$; $\Delta H = -1003$ kJ

Which of the following statements about this equation is *not* true?

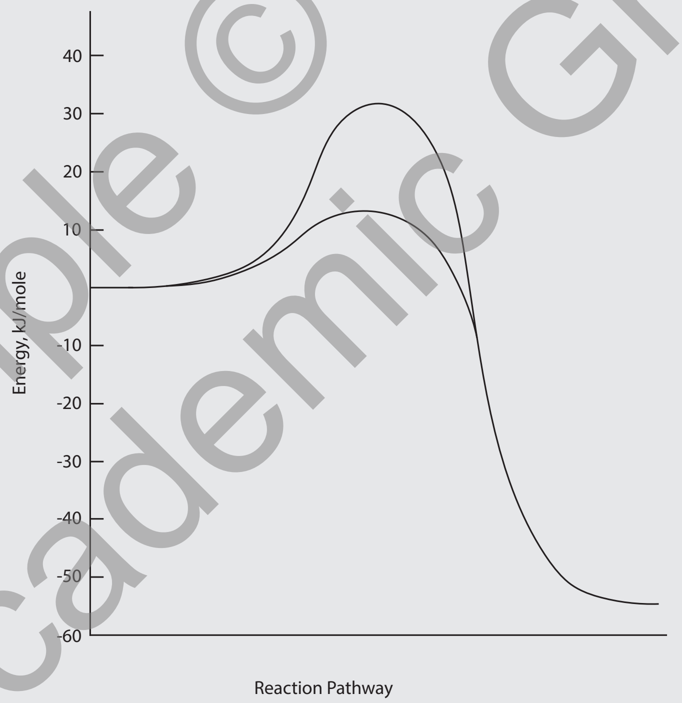
a) Aluminium chloride will be produced as a solution in water.

b) The reaction is exothermic.

c) Approximately 500 kJ of energy will be produced for each mole of aluminium used.

d) Aluminium and hydrochloric acid should be mixed in a 1:3 mole ratio before you could calculate the heat energy produced in any given situation.

Questions 4 to 7 are based on the following sketch:



4. The activation energy for the forward reaction, in the presence of the catalyst, in KJ mol^{-1} is about

a) 10 b) 30 c) 50 d) 60

5. In the uncatalysed reaction, the overall heat of reaction, ΔH, in kJ mol^{-1}, is

a) -10 b) -30 c) -50 d) -60

6. The activation energy for the reverse reaction, without a catalyst, in kJ mol^{-1}, is about

a) 10 b) 30 c) 50 d) 80

7. Which of the following is *false* for the reaction pathway in the presence of a catalyst?

a) The catalyst speeds up the rate of reaction for both the forward and the reverse processes.

b) The catalyst enables the reaction to proceed rapidly at a lower temperature.

c) The catalyst involves the formation of an activated complex.

d) The catalyst lowers the ΔH for the reaction.

Study the energy profile sketches presented below and answer questions 8 and 9.

8. Which reaction will be fastest at room temperature?

a) A b) B c) C d) D e) E

9. Which diagram is most likely to represent the burning of a candle?

a) A b) B c) C d) D e) E

10. A burning match is often used to start the combustion of natural gas in air because

a) an energy barrier must be overcome before the reaction can proceed.

b) ΔH for the reaction is larger than the energy available at room temperature.

c) the reaction is endothermic and must be driven by an external energy source.

d) the gas is too cold to burn spontaneously.

11. The activation energy of a reaction is usually

a) equal to the ΔH for the reaction.

b) equal to the sum of the energies of the reactants and the products.

c) decreased by the addition of a catalyst.

d) decreased by increasing the temperature of the system.

12. A catalyst in a chemical reaction

a) changes the activation energy of the reaction.

b) changes the rate of the forward reaction only.

c) decreases the rate of the back reaction.

d) increases the yield of the products in a reaction